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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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ON THE FEATURES OF STRESS RELAXATION IN ISOTACTIC CRYSTALLINE POLYPROPYLENE

The study of stress relaxation in isotactic crystalline polypropylene showed that the stress in deformed specimens disappears completely with time. On this basis it could be assumed that a process of plastic deformation develops in crystalline polypropylene. However, it turned out that the disappearance of stress is due to the appearance and development of cracks. Experiments with amorphous polypropylene showed that in this case (even at 20°) the stress in deformed specimens disappears completely with time, but this process is not accompanied by the formation of cracks. It became clear that the appearance of cracks in the process of stress relaxation is associated with the crystalline state of polypropylene (⌢1).

The conditions for the appearance and growth of cracks in polypropylene were determined by us earlier. It seemed essential to determine from what point in time cracks begin to appear in deformed specimens and how the growth of cracks affects the character of the relaxation curves. For this purpose, experiments were carried out to study stress relaxation in isotactic crystalline polypropylene in the deformed state (the specimens were stretched by 8% at 140°)*. At specified time intervals the experiments were interrupted and, with the aid of an optical microscope, the change in the surface of the specimens and the structure of the transverse sections was monitored.

Fig. 1. Dependence of stress on time at constant deformation. **1** –crystalline polypropylene (duration of experiments: *a* –5 min., *b* –30 min., *v* –1 hour, *g* –2 hours, *d* –3.5 hours). **2** –amorphous polypropylene. Curve 2 was obtained at 20° and a deformation of 15%. The stress in the specimen disappeared completely after 85 hours.

Figure 1 presents the overall relaxation curve (⌢1) of crystalline polypropylene obtained from this series of experiments, on which the durations of the experiments are marked. (It should be noted that the individual relaxation curves superpose well on one another.) As is seen from this curve, in the deformed specimens drops in stress are observed twice (a sharp one at short times and a less sharp one at longer times).

Microphotographs in polarized light of the deformed specimens shown in Fig. 2. These microphotographs show that the first cracks begin to appear in the specimens as early as 5 min after the start of the experiment. As was shown earlier (2), in these experiments as well the cracks are oriented perpendicular to the direction of action of the external tensile force.

The obtained transverse sections of the deformed specimens are shown in Fig. 3. As is evident from Fig. 3, with increasing duration of the experiment the number of cracks and their sizes increase.

Thus, stress relaxation in crystalline polypropylene (see Fig. 1, *1*) at short times of force action proceeds by the usual mechanism, both as a result of molecular rearrangements and because of crack development in the specimen. Another feature, clearly visible from Fig. 1, is the appearance of a second drop in stress on the relaxation curve at longer experiment durations (about 2.5–3.5 hr). This feature is also associated with the process of crack growth. From Fig. 3 it is evident that only after two hours of stress relaxation do the cracks have time to grow to sizes approaching the thickness of the specimen, and they become comparable with it only after relaxation for 3.5 hr. By the same time (see Fig. 2), many individual cracks join together into a single network of cracks. The considerable penetration of cracks into the depth of the specimen and their joining into a common network have as their obvious consequence a sharp decrease in the real cross-sectional area of the specimen.

Since the stress-relaxation experiment is conducted at a constant value of elongation, it is clear that a considerable decrease in the cross-sectional area must lead to a rapid decrease in the force necessary to maintain the prescribed deformation. In accordance with this, in the time region of about 2.5–3.5 hr (Fig. 1) a second drop in the nominal stress occurs. Naturally, the process of stress relaxation ultimately leads to destruction of the specimen (if the cracks grow through it) and the stress falls to zero.

In accordance with this, two types of completely relaxed specimens were obtained: cracked intact ones and ruptured ones. In conclusion, it is necessary to consider the influence of supermolecular structures on the process of stress relaxation in crystalline polypropylene. As is evident from Fig. 4, during crystallization of molten polypropylene films, previously held for 3.5 hr at 140° in a uniaxially stressed state, large spherulites arise, whereas from the melt of the original film smaller spherulites are obtained (Fig. 4a).

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* Carrying out the experiments at 140° made it possible to observe the processes of crack development and structure formation, which proceed most rapidly under these conditions.

Thus, in the process of stress relaxation at 140°, substantial changes occur in the supermolecular structures, manifested even upon recrystallization after melting of the film. It should be noted that in a film with large spherulites (Fig. 4), cracks arise both at the boundary and inside the spherulites (^{3}), which indicates the appearance of considerable internal stresses in such a film. Therefore it is quite obvious that the change in supermolecular structures during stress relaxation must influence the process of crack growth and, consequently, the course of the stress-relaxation process itself.

On the basis of the investigations carried out, it may be concluded that the occurrence of cracks when studying the relaxation properties of polypropylene is connected with its crystalline state, since no such phenomenon is observed in amorphous polypropylene. It may be assumed that the increase in the number and sizes of cracks is connected with the growth in size of the elements of the supermolecular structures in crystalline polypropylene that has remained for a long time in a deformed state at high temperature.*

* It should be noted that completely analogous phenomena are also observed at lower temperatures. Possibly in this case the increase in the sizes of the elements of the supermolecular structures will not be decisive, and the processes of crack development depend mainly on the magnitude of deformation and the time of action of the force.

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Fig. 2. Microphotographs of samples of crystalline polypropylene kept for different times in a stressed state (at 140° and 8% deformation). Duration of the experiments: *a* –5 min., *b* –3.5 hr.

Fig. 3. Microphotographs of transverse sections of samples of crystalline polypropylene kept for different times in a stressed state (at 140° and 8% deformation). 80×. Duration of the experiments: *a* –2 hr., *b* –3.5 hr.

Fig. 4. Microphotographs of films of crystalline polypropylene (thickness 30 μ). *a* –initial film, *b* –film pre-deformed at 140° for 3.5 hr.

The relaxation curve obtained, on which there are two regions of stress decrease at short and long times, makes it possible to suppose that at the beginning of the experiment rapid relaxation processes take place, which are usually observed upon stretching polymer samples. Then follows the process of crack development, the nuclei of which may exist in the initial crystalline film ($\widehat{\ }4$). The decrease in stress at the end of the experiment is undoubtedly connected with complex processes of structure formation that promote more rapid crack growth. For irreversible deformations to develop in such a system, large supramolecular formations must be displaced. The displacement of large structural elements may apparently occur under the action of very large forces exceeding the strength of the material ($\widehat{\ }5$).

Therefore, in crystalline polymers of the polypropylene type, in which supramolecular structures are very readily formed, the formation of cracks and their influence on the course of relaxation processes become understandable.

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